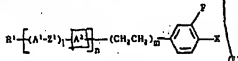


90-184497/25 E14 (25) (15) **INVER 25.11.89**
MERCK PATENT GMBH DE 3939-116-A
 07.12.88-DE-841120 (+DE-999116) (13.04.90) C07C-255/30
 C07D-309/04 C07B-319 C07D-335/02 C07D-339 C19A-10/14
 Fluoro-benzonitrile deriv. produ. by metallation of 3-substit.
 fluoro-benzene(s), followed by carboxylation or formylation and
 conversion into nitrile
 CNO-680923

(1) 3-Fluorobenzonitrile deriv. (I) of formula (I) (X = CN) are produced by metallation of the corresp. fluorobenzene deriv. (II) (X = H) to form the corresp. metal deriv. (III) (X = Li, Na or K), then carboxylating (III) and converting the carboxylic acid into (I) or formulating (III) and converting the resulting aldehyde into (I).



R¹ = up to 18C perfluoroalkyl, alkyl or alkynyl (opt. with one or more CH₂ gps. replaced by O, S or -C≡C-)

(7-05, 10-A15B, 10-A15D) (3-D1D1)

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A¹, A² = (a) 1,4-phenylene, (b) 1,4-cyclohexylene (opt. with 1 or 2 non-adjacent CH₂ gps. replaced by O or S) or (c) 1,4-cyclohexenylene, 1,4-bicyclo-[2,2,2]octylene or piperidine-1,4-diyl (with (c) and (b) opt. mono- or poly-substit. with H and/or Me);

Z¹ = -CH₂-CH₂-, -OCH₂-, -CH₂O- or single bond; n = 0, 1 or 2; m = 0 or 1; 1 + m = 1, 2, 3 or 4.
 (2) Cpd. (I) with A¹ = A² = 1,4-phenylene, Z¹ = -CH₂-CH₂- or single bond, 1 + m = 1, m = 0 or 1 (if m = 0, then Z¹ = -CH₂-CH₂-) are claimed as such.

USP/ADVANTAGES

(I) are useful as intermediates, esp. for the synthesis of liq. crystalline cpds., or as components of liq. crystalline phases (to improve dielectric anisotropy or other properties). The invention provides a regiospecific process for the prodn. of (I) in good yield.

DETAIL

(III) is, e.g. 4-R¹-3'-fluorobiphenyl, 3-fluoro-4'-R¹-cyclohexylbenzene, etc. (14 R¹-substit. starting cpds.

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Noted); metallation is carried out at -80 to -50°C with, e.g. n-BuLi, KNH₂ etc. in a solvent such as THF, dioxane, cyclohexane, toluene, etc. with NMPT etc. as activator.

EXAMPLE

10 ml. 0.1-M soln. of n-BuLi in hexane was added at -70°C to a mixt. of 0.1 mol. 3-(trans-4-heptylcyclohexyl)-fluorobenzene (prepd. as described in EP-119756) and 0.1 mol. tetrabutylstibylendiamine in 400 ml. THF, then the mixt. was stirred for 3 hrs. at -70°C, treated with a mixt. of 0.1 mol. N-formylpiperidine and 20 ml. THF, warmed to room temp. and worked up to give a solid prod., 0.1 mol. of the aldehyde obtd. was reacted with 0.15 mol. hydroxylamine O-sulphate acid as described in Helv. Chim. Acta 59, 2786 (1976) and worked up to give 4-(trans-4-heptylcyclohexyl)-3-fluorobenzonitrile as a colorless solid. The prod. had crystalline/melt transition pt., 19°C; nematic/isotropic transition pt., 21°C. (10pp1712DNDwgNo0/0).

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